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Ligand Stereochemistry in the Multiple Substitution of Bicapped Tetracobalt Clusters

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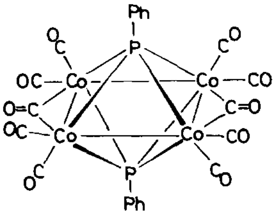
Abstract

The tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ undergoes multiple ligand substitution of up to four carbonyl ligands. The regio- and stereochemistry of CO replacement with the phosphorus(III) nucleophile $P(OMe)_3$ is established by the single crystal X-ray crystallography of the tris derivative. $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$ is successfully crystallized in the orthorhombic space group $Pna2_1$ with $a = 51.064$, $b = 13.000$ and $c = 12.407$ Å and $\rho = 1.65$ g cm^{-3} for $Z = 8$. The 1,2,3-substitution pattern of the tetracobalt cluster with syn/anti/syn stereochemistry affords in the unit cell two independent atropisomers as a result of restricted rotation about the phenyl–phosphinidene bond. The nature of the observed phosphite dispositions and the resulting structural perturbations of the tetracobalt cluster are discussed.

Introduction

The tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ and its phosphine derivatives have been employed as catalysts in olefin hydroformylation [1, 2]. Such polynuclear clusters are also of general interest since the multisite interaction between the tetracobalt core and the capping μ_4-phosphorus (and other chalcogen) moieties may serve as a paradigm for substrate activation in heterogeneous catalysts that possess square or rectangular metal packings in the surface layer [3, 4]. However, only limited structural information exists for the multiple substitution of the carbonyl ligands with phosphine activators in catalytically viable clusters such as $Co_4(CO)_{10}(PPh)_2$ (I).



I

Thus our recent study of the ligand substitution of I is opportune since it has provided us with a graded series of tetracobalt clusters which are polysubstituted with phosphorus(III) ligands [5, 6], *i.e.*

$$Co_4(CO)_{10}(PPh)_2 + nP(OMe)_3 \longrightarrow Co_4(CO)_{10-n}(PPh)_2[P(OMe)_3]_n + nCO \quad (1)$$

The molecular structures of the parent cluster I and the bis ($n = 2$) and tetrakis ($n = 4$) derivatives have been established by X-ray crystallography [5, 7, 8]. Owing to its unique crystallographic features, the structure of the tris ($n = 3$) derivative is presented here in detail separately.

Results and Discussion

Synthesis of the Tris-substituted Tetracobalt Cluster

The parent tetracobalt cluster I was treated with slightly more than three equivalents of trimethyl phosphite in benzene or toluene solution at >80 °C. The progress of the ligand substitution according to eqn. (1) was monitored by periodically extracting an aliquot of the reaction mixture for analysis. Optimum yields (30%) of the tris-substitution product were determined from the characteristic carbonyl stretching bands at 2020 and 1970 cm^{-1} in the IR spectra and from the thin-layer chromatograms (TLC). Better yields (55%) of the same product were obtained when the preformed bis-derivative was treated with one equivalent of trimethyl phosphite at 50 °C.

$$Co_4(CO)_8(PPh)_2[P(OMe)_3]_2 + P(OMe)_3 \longrightarrow Co_4(CO)_7(PPh)_2[P(OMe)_3]_3 + CO \quad (2)$$

Single crystals of the tris-derivative suitable for X-ray crystallography were successfully grown as dark red prisms from a 1:10 mixture (v/v) of toluene and n-hexane at −20 °C.

X-ray Crystallography of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$

The single crystal of the tris-derivative contained a pair of fully independent molecules in each asymmetric unit cell. These isomers **A** and **B** were readily differentiated by the dissimilar orientations of the

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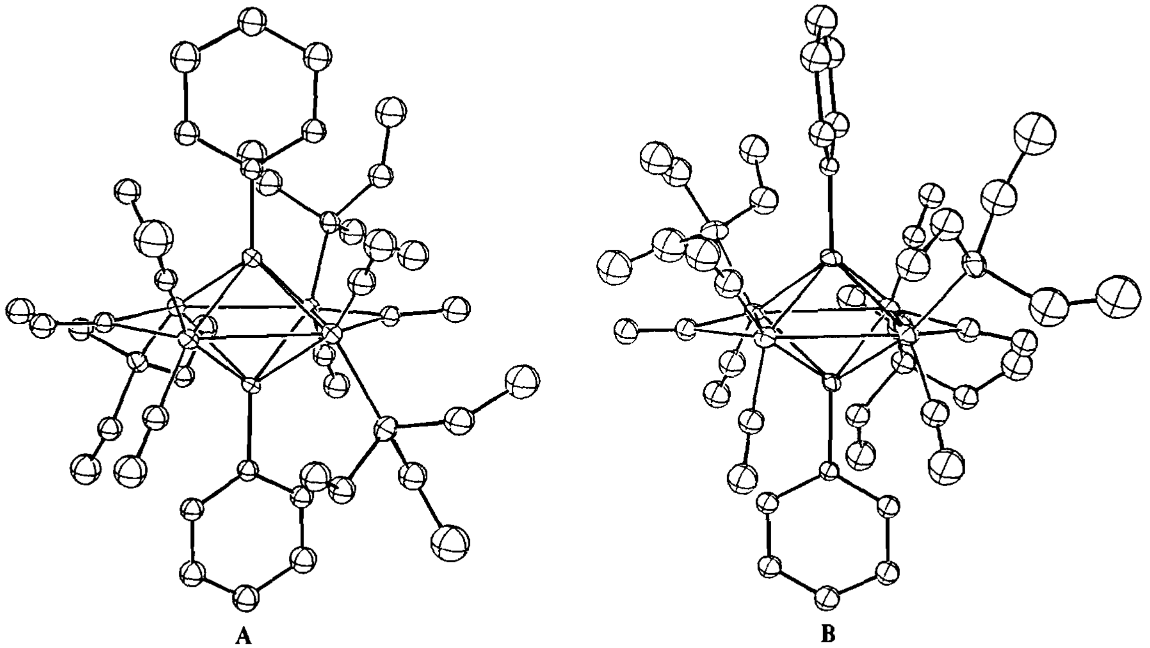
TABLE I. X-ray Crystallographic Data for $Co_4((CO)_7(PPh)_2$-$[P(OMe)_3]_3$

Space group	$Pna2_1$, orthorhombic
Cell constants	a = 51.064(16) Å b = 13.000(3) Å c = 12.407(3) Å
Volume (V)	8236.1 Å^3
Molecular formula	$C_{28}H_{37}Co_4P_5O_{16}$
Molecular weight	1020.2
Molecules per cell (Z)	8
Density (ρ)	1.65 g cm^{-3}
Absorption coefficient (μ)	18.4 cm^{-1}
Radiation Mo Kα (λ)	0.71073 Å
Collection range	$4° \leqslant 2\theta \leqslant 35°$
Scan width ($\Delta\theta$)	$(0.45 + 0.35 \tan \theta)°$
Maximum scan time (s)	90
Scan speed range (min^{-1})	0.50 to 6.7°
Total data collected	3013
Independent data, $I > 3\sigma(I)$	2485
Total variables	512
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o \rvert$	0.048
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{1/2}$	0.054
Weights	$w = 1.0$

phenyl planes. The X-ray data collection and process parameters for $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$ are included in Table I.

The ORTEP diagrams in Fig. 1 show the molecular configurations of both isomeric pairs, whose cores consist basically of four cobalt atoms in a rectangular array with the shorter sides bridged by μ_2-carbonyl groups. The capping of the cobalt tetramers by a pair of μ_4-phenylphosphinidene moieties completes the overall octahedral Co_4P_2 polyhedral core generally found in this genre of clusters [7–9]. The phosphite ligands are situated on three separate cobalt centers in an alternating arrangement in both **A** and **B**. This arrangement gives rise to the observed syn/anti/syn stereochemistry which allows for maximal interligand separation [10]. The selected bond lengths and bond angles for the pair of tri-substituted conformers **A** and **B** are compared in Tables II and III, respectively.

The four carbonyl-bridged Co–Co bond distances of 2.516 Å (av) in **A** and **B** compare well with the same bonds in **I** (2.520 Å) and with those in the bis- (2.524 Å) and the tetrakis- (2.520 Å) [5, 7, 13]. However the longer noncarbonyl-bridged Co–Co bonds in **A** and **B** are different from those in the analogues. Thus the noncarbonyl-bridged Co–Co bonds flanked by adjacent $P(OMe)_3$ ligands (*i.e.*, the syn/anti relation) are 2.747(2) and 2.764(2) Å for **A** and **B**, respectively, whereas the opposed bonds which are flanked by only one $P(OMe)_3$ ligand are 2.709(2) and 2.711(2) Å. The elongation of the weaker noncarbonyl-bridged Co–Co bonds in these conformers presumably results from unfavorable steric interactions within the cluster polyhedron induced by the disposition adopted by the phosphite ligands. [By comparison, the noncarbonyl bridged Co–Co bonds in the parent cluster **I** are 2.698 Å (av).]. A similar change in bond lengths arising from unfavorable intramolecular interactions in phosphine substituted clusters has been observed in $Co_4(CO)_8(PPh)_2(PPh_3)_2$ and $Co_4(CO)_8(PPh)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)$ [8, 11].



A **B**

Fig. 1. ORTEP diagram of the independent tri-substituted isomers in $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$ (IV) showing the 1,2,3-disposition of phosphite ligands with syn/anti/syn stereochemsitry. For clarity, the hydrogen atoms are not included.

TABLE II. Selected Bond Distances in $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$[a]

Conformer A	Distance (Å)	Conformer B	Distance (Å)
Co(1)–Co(2)	2.522(2)	Co(5)–Co(6)	2.512(2)
Co(2)–Co(3)	2.747(2)	Co(6)–Co(7)	2.764(2)
Co(3)–Co(4)	2.516(2)	Co(7)–Co(8)	2.512(2)
Co(4)–Co(1)	2.709(2)	Co(8)–Co(5)	2.711(2)
Co(1)–P(1)	2.272(3)	Co(5)–P(6)	2.227(3)
Co(2)–P(1)	2.255(3)	Co(6)–P(6)	2.226(3)
Co(3)–P(1)	2.312(3)	Co(7)–P(6)	2.221(3)
Co(4)–P(1)	2.256(3)	Co(8)–P(6)	2.267(3)
Co(1)–P(2)	2.237(3)	Co(5)–P(7)	2.256(3)
Co(2)–P(2)	2.247(3)	Co(6)–P(7)	2.261(3)
Co(3)–P(2)	2.226(3)	Co(7)–P(7)	2.294(3)
Co(4)–P(2)	2.286(3)	Co(8)–P(7)	2.269(3)
Co(1)–P(3)	2.146(3)	Co(5)–P(8)	2.143(3)
Co(2)–P(4)	2.159(3)	Co(6)–P(9)	2.160(3)
Co(3)–P(5)	2.150(3)	Co(7)–P(10)	2.155(3)
Co(1)–C(3)	1.693(11)	Co(5)–C(31)	1.733(11)
Co(2)–C(4)	1.650(11)	Co(6)–C(32)	1.772(11)
Co(3)–C(5)	1.688(10)	Co(7)–C(33)	1.721(14)
Co(4)–C(6)	1.751(10)	Co(8)–C(34)	1.755(11)
Co(4)–C(7)	1.729(11)	Co(8)–C(35)	1.787(13)
Co(1)–C(1)	1.896(10)	Co(5)–C(29)	1.933(10)
Co(2)–C(1)	1.847(10)	Co(6)–C(29)	1.880(10)
Co(3)–C(2)	1.899(10)	Co(7)–C(30)	1.901(9)
Co(4)–C(2)	1.962(10)	Co(8)–C(30)	1.937(10)
P(1)–C(17)	1.788(9)	P(6)–C(45)	1.821(10)
P(2)–C(23)	1.790(8)	P(7)–C(51)	1.839(10)
P(1)···P(2)	2.582(6)	P(6)···P(7)	2.548(6)

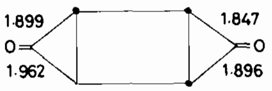
[a]Numbers in parentheses are estimated standard deviations in the least significant digit. For numbering scheme, see Fig. 3.

TABLE III. Selected Bond Angles in $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$[a]

Conformer A	Angle (°)	Confermer B	Angle (°)
Co(5)–Co(6)–Co(7)	89.15(5)	Co(1)–Co(2)–Co(3)	89.49(6)
Co(6)–Co(7)–Co(8)	89.63(6)	Co(2)–Co(3)–Co(4)	89.59(5)
Co(7)–Co(8)–Co(5)	90.36(5)	Co(3)–Co(4)–Co(1)	90.46(6)
Co(8)–Co(5)–Co(6)	90.83(6)	Co(4)–Co(1)–Co(2)	90.33(5)
Co(5)–P(6)–Co(6)	68.69(8)	Co(1)–P(1)–Co(2)	67.71(8)
Co(5)–P(6)–Co(7)	112.9(1)	Co(1)–P(1)–Co(3)	108.2(1)
Co(6)–P(6)–Co(7)	76.8(1)	Co(2)–P(1)–Co(3)	73.94(9)
Co(6)–P(6)–Co(8)	111.9(1)	Co(2)–P(1)–Co(4)	110.8(1)
Co(7)–P(6)–Co(8)	68.06(9)	Co(3)–P(1)–Co(4)	66.85(9)
Co(8)–P(6)–Co(5)	74.19(9)	Co(4)–P(1)–Co(1)	73.51(9)
Co(5)–P(7)–Co(6)	67.59(9)	Co(1)–P(2)–Co(2)	68.46(9)
Co(5)–P(7)–Co(7)	109.1(1)	Co(1)–P(2)–Co(3)	112.6(1)
Co(6)–P(7)–Co(8)	110.6(1)	Co(2)–P(2)–Co(4)	110.0(1)
Co(7)–P(7)–Co(8)	66.81(9)	Co(3)–P(2)–Co(4)	67.80(9)
Co(8)–P(7)–Co(5)	73.60(9)	Co(4)–P(2)–Co(1)	73.60(9)
P(6)–Co(5)–P(7)	69.3(1)	P(1)–Co(1)–P(2)	69.86(9)
P(6)–Co(6)–P(7)	69.2(1)	P(1)–Co(2)–P(2)	70.0(1)
P(6)–Co(7)–P(7)	68.7(1)	P(1)–Co(3)–P(2)	69.32(9)
P(6)–Co(8)–P(7)	68.4(1)	P(1)–Co(4)–P(2)	69.3(1)
P(6)–Co(5)–P(8)	167.1(1)	P(1)–Co(1)–P(3)	97.5(1)
P(7)–Co(5)–P(8)	98.0(1)	P(2)–Co(1)–P(3)	164.2(1)
P(6)–Co(6)–P(9)	97.1(1)	P(1)–Co(2)–P(4)	159.0(1)
P(7)–Co(6)–P(9)	157.5(1)	P(2)–Co(2)–P(4)	95.8(1)
P(6)–Co(7)–P(10)	160.6(1)	P(1)–Co(3)–P(5)	97.8(1)
P(7)–Co(7)–P(10)	98.5(1)	P(2)–Co(3)–P(5)	160.2(1)
Co(5)–C(29)–Co(6)	82.4(4)	Co(1)–C(1)–Co(2)	84.7(4)
Co(7)–C(30)–C(8)	81.8(4)	Co(3)–C(2)–Co(4)	81.3(4)
Co(5)–C(31)–O(31)	171.0(1)	Co(1)–C(3)–O(3)	174.0(1)
Co(6)–C(32)–O(32)	173.3(9)	Co(2)–C(4)–O(4)	176.0(1)
Co(7)–C(33)–O(33)	179.1(7)	Co(3)–C(5)–O(5)	176.0(8)
Co(8)–C(34)–O(34)	177.0(1)	Co(4)–C(6)–O(6)	174.9(9)
Co(8)–C(35)–O(35)	171.0(1)	Co(4)–C(7)–O(7)	176.8(9)

[a]Numbers in parentheses are estimated standard deviation in the last digit. See Fig. 3 for numbering scheme.

The five independent terminal Co–CO bond distances in both conformers vary from 1.650(11) to 1.787(13) Å with a mean distance of 1.728 Å. By way of contrast, the longer μ_2-bridging Co–CO distances range from 1.880(10) to 1.962(10) Å, as shown in the projections below.



A

B

[Note the cobalt atoms with a phosphite ligand are indicated with closed circles.] Both conformers show the expected shortening of the μ_2-bridging Co–CO bond lengths at the cobalt center substituted with a phosphite ligand in comparison with that at an unsubstituted site. The unsubstituted cobalt site in conformer **A** possesses a Co(4)–C(2)O distance of 1.962(10) Å which is ~0.08 Å longer than the average of the other μ_2-bridging Co–CO bond distances. Conformer **B** shows a similar, but less pronounced elongation (~0.03 Å) of the μ_2-bridging Co(8)–C(30)O bond. Such changes can be accounted for by the better σ-donating ability of the phosphite ligands (relative to carbonyl) which places a higher electron density at the site of ligand substitution. This manifests itself in a greater degree of π-back bonding and diminution of the length of the μ_2-bridging Co–CO bond [5, 8].

The Co–$P(OMe)_3$ distances in both **A** and **B** range from 2.143(3) to 2.160(3) Å with a mean distance of 2.153 Å (av) which is in good agreement with the values observed in the bis- and tetrakis-derivatives [5]. Both conformers show identical phosphite dispositions about the cluster polyhedron, as evidenced by the $(MeO)_3P$–Co–$P(OMe)_3$ torsion angles. For example we found the torsional angle across the carbonyl-bridged Co–Co bonds to be 97° and 95° in **A** and **B**.

The orientation of the phenyl rings bonded to the phosphinidene caps is of interest since it forms the basis of the observed atropisomerism in the solid state structure [12, 13]*. In both **A** and **B**, there is a considerable deviation away from the near 0° twist angle exhibited by the other structurally analogous clusters [5, 7, 8, 11, 14]. (The twist angle is defined as the dihedral angle between the phenyl planes.) In conformer **A**, the twist angle of the phenyl groups is ~23°, but in conformer **B** it is ~85°. In other words, the phenyl planes are more or less parallel in **A** but perpendicular in **B**. That phenyl group in **B** which departs from the preferred bisection of the μ_2-carbonyl bridged Co–Co bonds is the one that is on the same face of the tetracobalt plane as the 1,3-syn oriented phosphite ligands. The steric overcrowding with the 1,3-syn oriented phosphite ligands is doubtlessly responsible for the twisting of the juxtaposed phenyl group. The resulting destabilization of the cluster core was also observed in the bis-substituted 1,3-syn PPh_3 derivative $Co_4(CO)_8(PPh)_2(PPh_3)_2$ in which the larger PPh_3 ligands yielded only one conformer with a phenyl twist angle of 90° [8]. (The latter was also accompanied by a slight puckering of the tetracobalt core.) The presence of two conformers **A** and **B** thus accords with the reduced steric crowding by the smaller phosphite ligands.

The coexistence of conformers **A** and **B** leads to an unusually long (orthorhombic) unit cell in the crystal of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$. Furthermore the elongated *a*-axis of >50 Å is greater by a factor of almost four over either the *b*- or *c*-axis. Figure 2 shows the principal direction of the **A** conformers to lie along the *a*-axis in parallel sheets, which are mutually perpendicular to alternating sheets of the **B** conformer.

Experimental

Materials

The tetracobalt cluster $Co_4(CO)_8(\mu_4\text{-}PPh)_2$ was prepared from sodium tetracarbonylcobaltate and dichlorophenylphosphine [5]. The bis-derivative $Co_4(CO)_8(PPh)_2[P(OMe)_3]_2$ was prepared by ligand substitution of **I** with trimethyl phosphite (Aldrich) following the distillation two times from sodium under an argon atmosphere. Benzene was distilled from sodiobenzophenone and stored under argon.

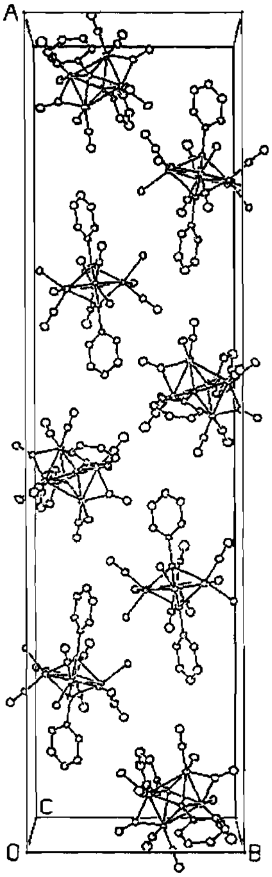


Fig. 2. Packing diagram for conformers A (along *a*-axis) and B (along *b*-axis) in the unit cell of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$. Note the methoxy groups and hydrogen atoms are omitted for clarity.

Synthesis of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$

To 1.0 g (0.0014 mol) of $Co_4(CO)_{10}(PPh)_2$ in 50 ml of benzene was added 0.6 ml (0.0048 mol) of $P(OMe)_3$. The reaction mixture was refluxed for 6.0 h, and then concentrated *in vacuo* to afford a red residue. Purification by chromatography with silica gel using benzene gave a red material free of other products, as shown by TLC. An analytically pure sample was recrystallized from a 1:10 mixture of toluene and hexane at −20 °C to yield 0.41 g (29% yield) of red $Co_4(CO)_7[P(OMe)_3]_3(PPh)_2$. IR ($CH_2Cl_2$), νCO: 2020(s), 1970(vs), 1810(m) cm^{-1}; UV (CH_2Cl_2), λ_{max}: 444 (ϵ 8348), 369 (ϵ 12648), 318 (ϵ 15529); *Anal.* Calc. for $C_{28}H_{27}Co_4P_5O_{16}$: C, 32.95; H, 3.63. Found: C, 32.90; H, 3.80%.

Alternatively, to 1.0 g (0.0011 mol) of $Co_4(CO)_8(PPh)_2[P(OMe)_3]_2$ in 50 ml of benzene was added 0.13 ml (0.0011 mol) of $P(OMe)_3$. The reaction mixture was heated at 50 °C overnight, and then allowed to cool to room temperature. Purification, as described above, afforded the tris-substituted cluster $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$ in 55% yield (0.62 g).

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*The solution behavior (^{13}C NMR) of this cluster has been briefly described [5] and the presence of the atropisomers in solution is under investigation. NMR ^{13}C spin lattice (T_1) studies are planned in order to assess the propensity of the phenyl groups to undergo anisotropic reorientation via rotation about the μ_4-phosphinidene–aryl bond.

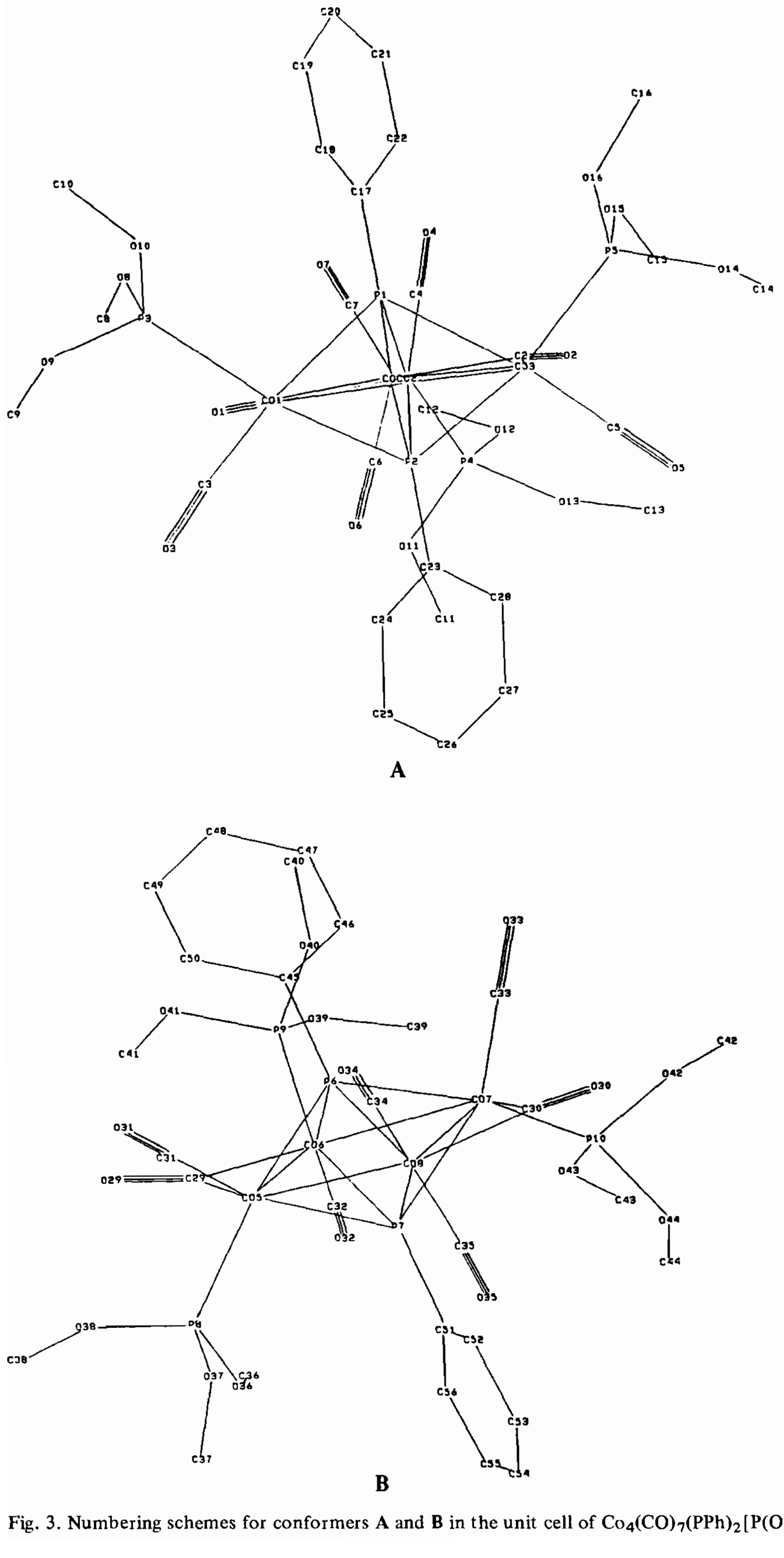

Fig. 3. Numbering schemes for conformers A and B in the unit cell of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$.

TABLE IV. Final Positional Parameters for the Non-hydrogen Atoms of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$[a]

Atom	*x*	*y*	*z*	*B* (Å²)
Co1	0.81905(5)	0.6669(2)	0.248	2.94(7)
Co2	0.81197(6)	0.8124(2)	0.1166(3)	2.82(7)
Co3	0.80794(5)	0.9467(2)	0.2867(3)	2.77(7)
Co4	0.81266(6)	0.7983(2)	0.4154(3)	2.91(7)
Co5	0.54548(6)	0.6878(2)	0.3026(3)	3.03(7)
Co6	0.58779(5)	0.7595(2)	0.2316(3)	3.16(7)
Co7	0.56221(6)	0.9414(2)	0.1845(3)	2.87(7)
Co8	0.52066(5)	0.8677(2)	0.2606(3)	2.87(7)
P1	0.7876(1)	0.7891(4)	0.2661(6)	2.8(1)
P2	0.8374(1)	0.8224(4)	0.2640(6)	2.7(1)
P3	0.7942(1)	0.5349(5)	0.2644(6)	3.9(2)
P4	0.8399(1)	0.8819(5)	0.0082(6)	3.6(2)
P5	0.7743(1)	1.0424(5)	0.2592(6)	3.5(2)
P6	0.5490(1)	0.7814(5)	0.1529(5)	2.7(2)
P7	0.5603(1)	0.8472(5)	0.3407(5)	3.0(2)
P8	0.5439(1)	0.6299(5)	0.4642(6)	4.5(2)
P9	0.6097(1)	0.7251(6)	0.0871(6)	4.3(2)
P10	0.5853(1)	1.0684(5)	0.2429(6)	4.8(2)
O1	0.8241(3)	0.613(1)	0.018(1)	5.1(4)*
O2	0.8049(3)	0.998(1)	0.514(1)	4.3(4)*
O3	0.8646(3)	0.556(1)	0.323(1)	5.9(4)*
O4	0.7682(3)	0.842(1)	−0.027(2)	6.0(4)*
O5	0.8435(3)	1.115(1)	0.249(2)	5.3(4)*
O6	0.8586(4)	0.759(2)	0.552(2)	8.1(5)*
O7	0.7755(3)	0.731(1)	0.577(2)	6.0(4)*
O8	0.7788(3)	0.516(1)	0.376(1)	4.5(4)*
O9	0.8077(3)	0.426(1)	0.258(2)	4.7(4)*
O10	0.7710(3)	0.528(1)	0.183(1)	5.2(4)*
O11	0.8642(3)	0.815(1)	−0.019(1)	4.6(4)*
O12	0.8295(3)	0.918(1)	−0.108(2)	6.2(5)*
O13	0.8508(3)	0.989(1)	0.046(2)	5.9(4)*
O14	0.7787(3)	1.164(1)	0.274(1)	4.7(4)*
O15	0.7619(3)	1.043(1)	0.141(1)	4.2(4)*
O16	0.7493(3)	1.019(1)	0.330(1)	4.5(4)*
O29	0.5872(3)	0.539(1)	0.273(2)	5.5(4)*
O30	0.5172(3)	1.077(1)	0.174(1)	4.5(4)*
O31	0.5063(4)	0.550(1)	0.216(2)	8.1(5)*
O32	0.6357(3)	0.787(1)	0.359(1)	5.5(4)*
O33	0.5747(3)	0.983(1)	−0.038(2)	6.6(5)*
O34	0.4757(3)	0.796(1)	0.137(1)	5.7(4)*
O35	0.4877(3)	0.945(1)	0.436(2)	6.7(5)*
O36	0.5244(3)	0.672(1)	0.549(2)	6.2(5)*
O37	0.5705(4)	0.643(2)	0.529(2)	8.7(6)*
O38	0.5380(4)	0.508(2)	0.460(2)	9.2(6)*
O39	0.6383(3)	0.770(1)	0.080(2)	6.1(5)*
O40	0.5963(3)	0.762(1)	−0.020(1)	5.2(4)*
O41	0.6158(3)	0.608(1)	0.057(1)	5.5(4)*
O42	0.5937(5)	1.151(2)	0.161(2)	10.6(7)*
O43	0.6144(3)	1.035(1)	0.272(2)	6.9(5)*
O44	0.5778(4)	1.142(1)	0.341(2)	7.1(5)*
C1	0.8192(4)	0.675(2)	0.095(2)	3.1(5)*
C2	0.8074(4)	0.946(2)	0.440(2)	2.9(5)*
C3	0.8461(4)	0.601(2)	0.287(2)	4.6(6)*
C4	0.7863(4)	0.830(2)	0.038(2)	4.0(6)*
C5	0.8295(4)	1.043(2)	0.265(2)	3.7(5)*
C6	0.8402(4)	0.780(2)	0.497(2)	2.9(5)*
C7	0.7899(4)	0.758(2)	0.510(2)	4.0(6)*
C8	0.7925(5)	0.493(2)	0.474(2)	4.9(6)*
C9	0.8221(6)	0.390(2)	0.176(3)	7.0(8)*
C10	0.7521(6)	0.444(3)	0.187(3)	8.8(9)*
C11	0.8874(6)	0.852(2)	−0.070(3)	7.4(8)*
C12	0.8222(6)	0.839(2)	−0.186(3)	8.1(9)*
C13	0.8557(6)	1.083(2)	−0.014(3)	7.7(9)*
C14	0.7874(5)	1.209(2)	0.370(2)	5.8(7)*
C15	0.7766(5)	1.088(2)	0.048(3)	6.2(7)*
C16	0.7246(6)	1.073(2)	0.321(3)	7.6(8)*
C17	0.7529(4)	0.770(2)	0.268(2)	3.3(5)*
C18	0.7405(4)	0.725(2)	0.182(2)	4.0(6)*
C19	0.7133(5)	0.707(2)	0.177(2)	5.4(6)*
C20	0.6986(5)	0.738(2)	0.269(2)	5.5(6)*
C21	0.7106(5)	0.787(2)	0.353(2)	5.0(6)*
C22	0.7377(4)	0.802(2)	0.354(2)	3.9(6)*
C23	0.8722(4)	0.838(2)	0.273(2)	3.1(5)*
C24	0.8891(4)	0.779(2)	0.217(2)	3.7(5)*
C25	0.9161(4)	0.784(2)	0.226(2)	4.9(6)*
C26	0.9255(4)	0.853(2)	0.296(2)	4.8(6)*
C27	0.9100(5)	0.919(2)	0.358(2)	5.6(7)*
C28	0.8823(4)	0.912(2)	0.344(2)	4.0(6)*
C29	0.5790(4)	0.625(2)	0.273(2)	4.5(5)*
C30	0.5281(4)	0.999(2)	0.194(2)	3.3(5)*
C31	0.5236(4)	0.600(2)	0.248(2)	5.1(6)*
C32	0.6158(4)	0.778(2)	0.314(2)	4.0(6)*
C33	0.5696(5)	0.965(2)	0.052(2)	6.1(7)*
C34	0.4938(4)	0.826(2)	0.184(2)	4.2(6)*
C35	0.5024(5)	0.919(2)	0.371(2)	5.1(6)*
C36	0.4966(5)	0.678(2)	0.530(2)	6.1(7)*
C37	0.5752(7)	0.628(3)	0.640(3)	11*
C38	0.5406(7)	0.428(3)	0.512(3)	11*
C39	0.6427(6)	0.874(2)	0.084(3)	7.3(8)*
C40	0.6053(6)	0.742(3)	−0.125(3)	8.2(9)*
C41	0.6351(6)	0.555(3)	0.113(3)	9(1)*
C42	0.5762(7)	1.212(3)	0.117(3)	11(1)*
C43	0.6356(6)	1.100(2)	0.314(3)	7.5(8)*
C44	0.5554(6)	1.145(2)	0.401(3)	7.7(9)*
C45	0.5373(4)	0.733(2)	0.024(2)	2.8(5)*
C46	0.5254(4)	0.799(2)	−0.050(2)	3.6(5)*
C47	0.5167(4)	0.760(2)	−0.143(2)	4.0(6)*
C48	0.5195(5)	0.660(2)	−0.165(2)	4.7(6)*
C49	0.5317(5)	0.591(2)	−0.103(2)	4.5(6)*
C50	0.5409(4)	0.628(2)	−0.004(2)	4.1(6)*
C51	0.5682(4)	0.897(2)	0.476(2)	2.5(5)*
C52	0.5930(5)	0.930(2)	0.498(2)	5.0(6)*
C53	0.5984(5)	0.977(2)	0.599(3)	6.9(8)*
C54	0.5797(5)	0.977(2)	0.673(3)	6.3(7)*
C55	0.5562(5)	0.945(2)	0.657(2)	5.4(7)*
C56	0.5493(5)	0.900(2)	0.559(2)	4.3(6)*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Asterisk identifies atom refined isotropically.

X-ray Diffraction Study of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$

Crystals of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$ suitable for diffraction analysis were obtained by the slow evaporation of a hexane solution of the tris-substituted cluster. A large irregular block of approximate dimensions 0.90 × 0.50 × 0.40 mm was cut from a bigger dark red crystal and mounted on an Enraf-Nonius CAD-4 automatic diffractometer. The radiation used was Mo Kα monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Determination of unit cell constants was somewhat more difficult than normal due to the presence of a very long axis. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. The Laue symmetry was determined to be *mmm*, and the space group was shown to be either *Pnma* or $Pna2_1$. Intensities were measured using the omega scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. It was impossible to collect data with the usual θ–2θ method since the extreme length of the *a*-axis caused severe peak overlap along the lattice rows. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and did not vary significantly. In reducing the data, Lorentz and polarization factors were applied. However no absorption correction was made since the crystal dimensions were not too disparate and the absorption coefficient was not that large.

Even using the omega scan technique, many reflections were found to have highly uneven backgrounds indicative of mismeasurement. Thus approximately 150 reflections, as well as the systematic absences, were eliminated from the data before processing was completed. Since there were known to be eight molecules in the unit cell, it was initially assumed that the centrosymmetric space group *Pnma* was the correct choice. Although this eventually proved to be incorrect, it was still possible to solve the structure since the eight Co atoms in the asymmetric unit do indeed have essentially mirror symmetry. It made the solution appear to be two half-molecules each having two Co atoms on a mirror plane. After several unsuccessful attempts using various methods, the structure was finally solved (in the wrong space group) from the Patterson. This was only made possible by the extremely fortuitous positioning of one of the two independent molecules [Co(1)–Co(4)] such that all four Co atoms lay in one *yz* plane with the diagonals of the square plane essentially colinear with the *y* and *z* axes (see list of atomic coordinates). For the numbering schemes, see Fig. 3.

Since the dimensions of this plane were well known from our previous work on similar compounds [5, 14], it was soon found that two vectors in the Patterson map having length 3.5 Å, namely 0.00, 0.00, 0.27 and 0.00, 0.28, 0.00, corresponded to the diagonals. Confirmation of the $2x$, $2y$, $2z$ peak for Co(1) in the list allowed the other three Co and two capping P atoms in this particular molecule to be assigned coordinates also. At this point (since it was realized that the proposed structure of this molecule based on spectral results precluded internal mirror symmetry), the space group was changed to $Pn2_1a$ and the remaining atoms were quickly located in difference Fourier syntheses. There are two full independent molecules in the asymmetric unit possessing dissimilar phenyl rotations.

At the conclusion of isotropic refinement, the data and atomic coordinates were converted to the conventional setting of $Pna2_1$. Conversion to anisotropic thermal parameters for the 18 heavy atoms was accomplished, after which all hydrogens were entered in ideally calculated positions and held fixed. In order to minimize variables in this 180-atom refinement, it was necessary to keep all other atoms except Co and P isotropic. In order to fix the sense of rotation in this polar space group, refinement of the inverse coordinates was also done. Based on $+++/---$ *R* values of 5.9%/5.8%, the inverse set was chosen and all tables are based on these coordinates. After all shifts/e.s.d. ratios were less than 0.3, the full-matrix least squares converged at the agreement factors listed in Table I. Anomalous dispersion coefficients for the heavier elements were included. No unusually high correlations were noted between any of the variables in the last cycle of least squares refinement, and the final difference density map was featureless. All calculations were made using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. The final fractional position parameters are listed in Table IV.

Supplementary Material

Lists of the structure factor amplitudes, calculated atomic coordinates for the hydrogens, bond lengths and bond angles are available on request.

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